# Ion-Molecule Reactions in Electric Discharges

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Before the development of good vacuum equipment and techniques, mass spectrometrists observed many ions occurring at masses well above those of the molecules admitted to the instrument. These interfered with the main interests of the experimenters at that time, although in a few instances it was recognized that reactions were occurring between primary ions and molecules. When good vacuum facilities became available in the early 1930s they were adapted to mass spectrometry and for a number of years every effort was made to maintain pressures well below 10^{-6} torr in order to avoid collisions of primary ions with neutrals. However, in 1940, Mann, Hustrulid and Tate (1), in studying water, observed an ion at mass 19, and by vary-

(1) Mann, M.M., Hustrulid, A. and Tate, J. T., $\underline{Phys.}$ $\underline{Rev.}$, $\underline{58}$, 340 (1940)

ing the pressure in their instrument, concluded that it was H_3O^+, probably formed by the reaction:

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$
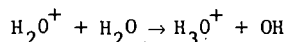
During the middle 50s, several groups of mass spectrometrists became curious as to the results that would be observed if source pressures were raised sufficiently to allow a few collisions to occur between ions and molecules. Several ions occurring at masses above those of the parent ion were observed. Because of this, a number of systematic studies were made and increasing interest and emphasis on reactions of ions with neutral molecules has developed, until at present some 50 to 100 papers per year are published on this subject alone.

Perhaps one of the strongest reasons for the interest in ion-molecule reactions is the fact that ions of unusual and unsuspected composition were observed. Most fascinating of these has been CH_5^+, which was completely unexpected, but which, nevertheless, is now well established as a stable ion. This ion was first announced by Tal'roze and Lyumbimova (2), but it was also reported shortly after the Russians

(2) Tal'roze, V. L. and Lyumbimova, A. K., $\underline{Dokl.}$ $\underline{Akad.}$ $\underline{Nauk}$ $\underline{SSSR}$, $\underline{86}$, 909 (1952)

by several groups in this country (3,4,5,9). Studies of secondary ions from a large number of molecules followed.

(3) Field, F. H., Franklin, J. L. and Lampe, F. W., $\underline{J.}$ $\underline{Amer.}$ $\underline{Chem.}$ $\underline{Soc.}$, $\underline{79}$, 2419 (1957)

(4) Stevenson, D. P. and Schissler, D. O., $\underline{J.}$ $\underline{Chem.}$ $\underline{Phys.}$, $\underline{23}$, 1353 (1955)

(9) Schissler, D. O. and Stevenson, D. P., $\underline{J.}$ $\underline{Chem.}$ $\underline{Phys.}$, $\underline{24}$, 926 (1956)

(5) Meisels, G. G., Hamill, W. H. and Williams, R. R., Jr., $\underline{J.}$ $\underline{Chem.}$ $\underline{Phys.}$, $\underline{25}$, 790 (1956)

The earlier studies of secondary ions were largely limited to ions of masses greater than that of the parent ion, but subsequent studies have shown that many secondaries of lower mass also occur. In most instances, the fact that the ion resulted from collision rather than from impurities was demonstrated by varying the pressure in the ion source. If the ion intensity increased as a second power of the pressure, the ion clearly resulted from a collision.

Having established that an ion was indeed the result of a collision, it was obviously of interest to ascertain the primary ion precursor of the secondary ion. Two methods have usually been used for this purpose. The method most often used was to measure the appearance potential of the secondary ion and compare it to appearance potentials of various primary ions occurring in the system in question.

Obviously, the secondary ion must have the same appearance potential as its precursor, and where reasonable agreement of primary and secondary ion appearance potentials was found the identities of reactant and product were established. In some instances, it has been possible to reduce the electron energy to the point where only one or two primary ions were present. Under these conditions, it is often possible by comparing intensities of secondary ions with the disappearance of primaries to identify unequivocally the precursors of the various secondaries. Obviously, both of these techniques suffer from certain difficulties. Where the primary ion spectrum is sufficiently complicated, or where the appearance potentials of several primary ions are sufficiently close together, it is very difficult and often impossible to determine the precursor of a secondary ion satisfactorily. Further, comparison of primary and secondary appearance potentials usually serves to identify only the precursor of lowest appearance potential. Possible precursors of higher appearance potential are obscured and can only be detected by other means. Of course, it is also true that one cannot always simplify the primary spectrum sufficiently by reducing the electron energy to permit satisfactory identification of the precursor. As a result, in recent years a few mass spectrometrists following Lindholm (6) have employed a primary mass sorter to select the primary ion which is then injected into the gas

(6)   For a survey of Lindholm's work see E. Lindholm, "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series 58, American Chemical Society, Washington, D. C., 1966, pl.

with which reaction is desired.

Mass spectrometer ion sources are quite small chemical reactors. It can easily be shown that the reaction time of an ion in the source will normally be in the order of a microsecond, and unless the pressure in the source is well over 100 torr only a small fraction of the ions can undergo collision. It early became apparent that where secondary ions were observed they must, in most instances, have resulted at almost every collision of ion and neutral. Further, in many instances, the heats of formation of ions and neutrals were well established, and in all such instances it was possible to show that the reactions were exothermic. Indeed, it would be impossible under most circumstances to observe a reaction to form secondary ions if the reaction were endothermic. Such endothermicity would appear as activation energy, which would greatly reduce the probability of reaction when the ion and molecule collide. (Later on we mention certain conditions in which this rule is violated, but under most circumstances it holds rigorously.) This rule is so seldom violated that it can be used as a means of helping to eliminate possible precursors of a secondary ion.

It was mentioned above that the secondary ions first observed occurred at masses above those of the parent. However, there was always an expectation that ions of lower mass might also be formed in collision reactions and as the pressure that could be tolerated in the ion source was increased it became apparent that such was indeed the case. For example, it was observed by Munson, Franklin and Field (7)

(7)   M.S.B.Munson, J. L. Franklin and F. H. Field, J. Phys. Chem. 68, 3098 (1964)

that the $C_2H_5^+$ ion from ethane and the $C_3H_7^+$ ion from propane, both present in the primary spectrum, increased with increasing pressure and indeed, in the case of propane the $C_3H_7^+$ ion increased from a very small proportion of the primary spectrum until it represented some 70% of all the ions present. Many secondary ions of mass less than the parent did not show such spectacular increases and other techniques were sought to establish these. One method of especial interest was that due to Cermak. (8). He employed electrons having energies too small to ionize in the

(8)   V. Cermak and Z. Herman, Collection Czechoslov. Chem. Commun. 27, 406 (1962)
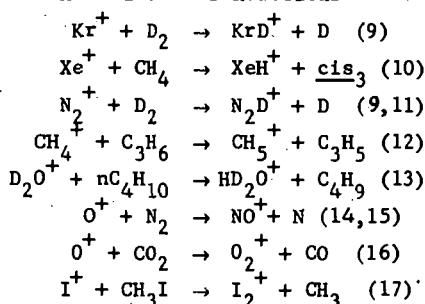
ionization chamber. However, he employed a relatively high variable potential between the ion chamber and the trap anode, so that the electrons were accelerated

in the anode region. Some of these ionized molecules present in that region and the ions were repelled by the potential on the anode and drifted back into the ionization chamber. These primary ions could not be themselves collected, but new secondary ions could be unequivocally identified. Further, by varying the potential on the anode, it was possible to obtain an appearance potential for the secondary ions and from this to deduce the identity of its precursor.

A large number of reactions of ions with neutrals have now been identified and typical examples of the various classes of such bimolecular reactions are given in tables 1 through 7.
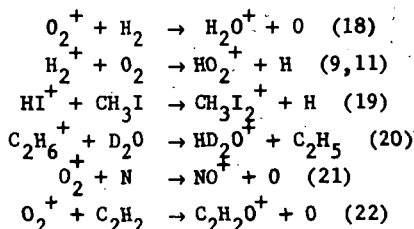
Table 1

Atom Transfer Reactions

$$Kr^+ + D_2 \rightarrow KrD^+ + D \quad (9)$$
$$Xe^+ + CH_4 \rightarrow XeH^+ + \underline{cis}_3 \quad (10)$$
$$N_2^+ + D_2 \rightarrow N_2D^+ + D \quad (9,11)$$
$$CH_4^+ + C_3H_6 \rightarrow CH_5^+ + C_3H_5 \quad (12)$$
$$D_2O^+ + nC_4H_{10} \rightarrow HD_2O^+ + C_4H_9 \quad (13)$$
$$O^+ + N_2 \rightarrow NO^+ + N \quad (14,15)$$
$$O^+ + CO_2 \rightarrow O_2^+ + CO \quad (16)$$
$$I^+ + CH_3I \rightarrow I_2^+ + CH_3 \quad (17)$$

(9) Schissler, D. O. and Stevenson, D. P., _J. Chem. Phys._, 24, 926 (1956)

(10) Field, F. H., Franklin, J. L., _J. Am. Chem. Soc._ 83, 4509 (1961)

(11) Stevenson, D. P., _J. Phys. Chem._, 61, 1453 (1957)

(12) Frankevich, E. L. and Tal'roze, V. L., _Dokl. Akad. Nauk SSSR_ 119, 1174 (1958)

(13) Lampe, F. W., Field, F. H. and Franklin, J. L., _J. Amer. Chem. Soc._, 79, 6132 (1957)

(14) Potter, R. F., _J. Chem. Phys._, 23, 2462 (1955)

(15) Fehsenfeld, F. C., Schmeltekopf, A. L. and Ferguson, E. E., _Planet. Space Science_ 13, 219 (1965)

(16) Fehsenfeld, F. C., Ferguson, E. E. and Schmeltekopf, A. L., _J. Chem. Phys._ 44, 3022 (1966)

(17) Pottie, R. F., Barker, R. and Hamill, W. H., _Radiation Research_ 10, 664 (1940)

Table 2

Positive Atomic Ion Transfer Reactions

$$O_2^+ + H_2 \rightarrow H_2O^+ + O \quad (18)$$
$$H_2^+ + O_2 \rightarrow HO_2^+ + H \quad (9,11)$$
$$HI^+ + CH_3I \rightarrow CH_3I_2^+ + H \quad (19)$$
$$C_2H_6^+ + D_2O \rightarrow HD_2O^+ + C_2H_5 \quad (20)$$
$$O_2^+ + N \rightarrow NO^+ + O \quad (21)$$
$$O_2^+ + C_2H_2 \rightarrow C_2H_2O^+ + O \quad (22)$$
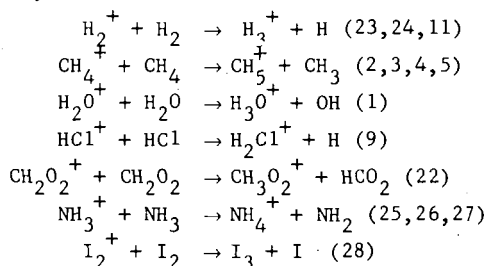
(18) Hutchinson, D. A., Paper presented at American Chemical Society Meeting, Minneapolis, Minnesota, September, 1955

(19) Pottie, R. F., Barker, R. and Hamill, W. H., _Radiation Research_ 10, 664 (1959)

(20) Lampe, F. W., Field, F. H. and Franklin, J. L., _J. Amer. Chem. Soc._, 79, 6132 (1957)

(21) Goldan, P. D., Schmeltekopf, A. L., Fehsenfeld, F. C., Schiff, H. I., and Ferguson, E. E., _J. Chem. Phys._ 44, 4095 (1966)

(22) Franklin, J. L., Munson, M.S.B., Tenth Symposium (International) on Combustion, The Combustion Institute, 1965, p. 561
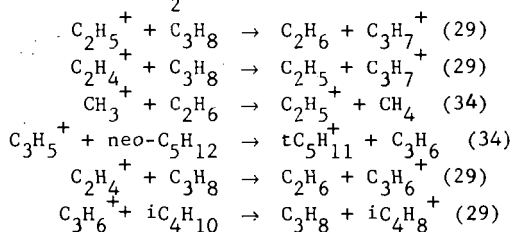
Table 3

Symmetrical Transfer Reactions

$$H_2^+ + H_2 \rightarrow H_3^+ + H \quad (23,24,11)$$
$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \quad (2,3,4,5)$$
$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \quad (1)$$
$$HCl^+ + HCl \rightarrow H_2Cl^+ + H \quad (9)$$
$$CH_2O_2^+ + CH_2O_2 \rightarrow CH_3O_2^+ + HCO_2 \quad (22)$$
$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2 \quad (25,26,27)$$
$$I_2^+ + I_2 \rightarrow I_3^+ + I \quad (28)$$

(23) Eyring, H., Hirschfelder, J. O. and Taylor, H. S., J. Chem. Phys. 4, 479 (1936)
(24) Stevenson, D. P. and Schissler, D. O., J. Chem. Phys. 23, 1353 (1955)
(25) Lampe, F. W. and Field, F. H., Tetrahedron 7, 189 (1959)
(26) Dorfman, L. M. and Noble, P. C., J. Phys. Chem. 63, 980 (1959)
(27) Derwish, G. A. W., Galli, A., Giardini-Guidoni, A., and Volpi, G. G., J. Chem. Phys. 39, 1599 (1963)
(28) Hogness, T. R. and Harkness, R. W., Phys. Rev. 32, 784 (1928)

Table 4
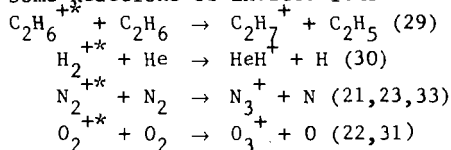
H$^-$ and H$_2^-$ Transfer Reactions

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+ \quad (29)$$
$$C_2H_4^+ + C_3H_8 \rightarrow C_2H_5 + C_3H_7^+ \quad (29)$$
$$CH_3^+ + C_2H_6 \rightarrow C_2H_5^+ + CH_4 \quad (34)$$
$$C_3H_5^+ + neo\text{-}C_5H_{12} \rightarrow tC_5H_{11}^+ + C_3H_6 \quad (34)$$
$$C_2H_4^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_6^+ \quad (29)$$
$$C_3H_6^+ + iC_4H_{10} \rightarrow C_3H_8 + iC_4H_8^+ \quad (29)$$

(29) M.S.B.Munson, J. L. Franklin and F. H. Field, J. Phys. Chem. 68, 3098 (1964)

Table 5

Some Reactions of Excited Ions

$$C_2H_6^{+*} + C_2H_6 \rightarrow C_2H_7^+ + C_2H_5 \quad (29)$$
$$H_2^{+*} + He \rightarrow HeH^+ + H \quad (30)$$
$$N_2^{+*} + N_2 \rightarrow N_3^+ + N \quad (21,23,33)$$
$$O_2^{+*} + O_2 \rightarrow O_3^+ + O \quad (22,31)$$

(30) H. von Koch and L. Friedman, J. Chem. Phys. 38, 115 (1963)
(31) R. K. Curran, J. Chem. Phys. 38, 2974 (1963)
(32) M.S.B.Munson, F. H. Field and J. L. Franklin, J. Chem. Phys. 37, 1790 (1962)
(33) M. Saporoschenko, Phys. Rev. 111, 1550 (1958)
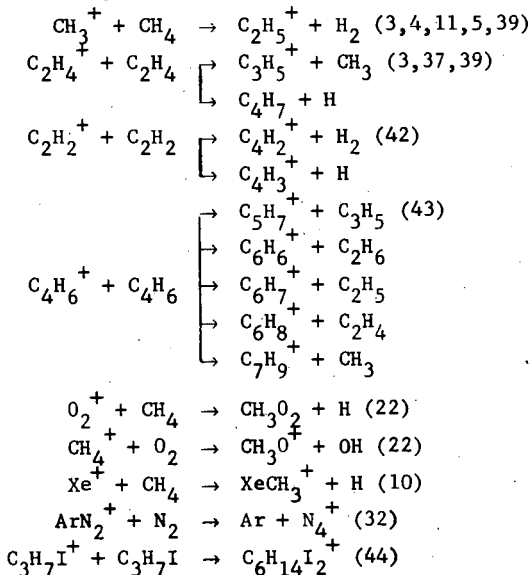(34) Field, F. H. and Lampe, F. W., J. Amer. Chem. Soc., 80, 5587 (1958)

Table 6

Charge Transfer Reactions

$$O^+ + O_2 \rightarrow O_2^+ + O \quad (35)$$

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+ \quad (36)$$

$$C_2H_2^+ + C_2H_4 \rightarrow C_2H_4^+ + C_2H_2 \quad (37)$$

$$Xe^+ + C_2H_4 \quad \left[\begin{array}{l} \rightarrow C_2H_4^+ + Xe \quad (38) \\ \rightarrow C_2H_2^+ + H_2^+ + Xe \quad (38) \end{array} \right.$$

$$Ar^+ + C_2H_4 \quad \left[\begin{array}{l} \rightarrow C_2H_2^+ + H_2 + Ar \quad (38) \\ \rightarrow C_2H_3^+ + H + Ar \quad (38) \end{array} \right.$$

$$Ar^+ + CH_4 \rightarrow CH_3^+ + H + Ar \quad (5,39)$$

$$F^+ + CO \quad \left[\begin{array}{l} \rightarrow CO^+ + F \quad (40) \\ \rightarrow C^+ + O + F \quad (40) \end{array} \right.$$
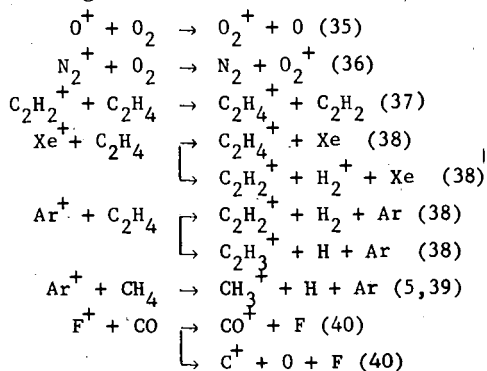
(35) F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf and E. E. Ferguson, _Planet. Space Sci._ _13_, 579 (1965)

(36) F. C. Fehsenfeld, A. L. Schmeltekopf and E. E. Ferguson, _Planet. Space Sci._ _13_, 919 (1965)

(37) F. H. Field, _J. Am. Chem. Soc._ _83_, 1523 (1961)

(38) J. L. Franklin and F. H. Field, _J. Am. Chem. Soc._ _83_, 3555 (1961)

(39) G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., _J. Phys. Chem._ 61, 1456 (1957)

(40) E. Lindholm, _Arkiv Fysik_ _8_, 433 (1954)

Table 7

Complex Rearrangements

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad (3,4,11,5,39)$$

$$C_2H_4^+ + C_2H_4 \quad \left[\begin{array}{l} \rightarrow C_3H_5^+ + CH_3 \quad (3,37,39) \\ \rightarrow C_4H_7^+ + H \end{array} \right.$$

$$C_2H_2^+ + C_2H_2 \quad \left[\begin{array}{l} \rightarrow C_4H_2^+ + H_2 \quad (42) \\ \rightarrow C_4H_3^+ + H \end{array} \right.$$

$$C_4H_6^+ + C_4H_6 \quad \left[\begin{array}{l} \rightarrow C_5H_7^+ + C_3H_5 \quad (43) \\ \rightarrow C_6H_6^+ + C_2H_6 \\ \rightarrow C_6H_7^+ + C_2H_5 \\ \rightarrow C_6H_8^+ + C_2H_4 \\ \rightarrow C_7H_9^+ + CH_3 \end{array} \right.$$

$$O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H \quad (22)$$

$$CH_4^+ + O_2 \rightarrow CH_3O^+ + OH \quad (22)$$

$$Xe^+ + CH_4 \rightarrow XeCH_3^+ + H \quad (10)$$

$$ArN_2^+ + N_2 \rightarrow Ar + N_4^+ \quad (32)$$

$$C_3H_7I^+ + C_3H_7I \rightarrow C_6H_{14}I_2^+ \quad (44)$$

(44) Pottie, R. F. and Hamill, W. H., _J. Phys. Chem._ _63_, 877 (1959)

(42) Field, F. H., Franklin, J. L. and Lampe, F. W., _J. Amer. Chem. Soc._, _79_, 2665

(43) Barker, R., Williams, R. R., Jr. and Hamill, W. H., presented at meeting of ASTM Committee E-14 on Mass Spectrometry, New Orleans, Louisiana, June 2-6, 19

Tables 1-6 present examples of relatively simple reactions. However, reactions involving quite profound changes in structure and bond reorganizations have been observed by a number of investigators. Table 7 shows several of these, which are given as typical examples. Certain of the reactions shown result in more than one set of products, all of which apparently occur at the same appearance potential and thus involve the same precursor. Of course, the intensities of the product ions will, in most instances, not be the same. One would expect that reactions of this kind would involve the formation of a relatively stable complex, which breaks up in ways dictated by the energy content of the complex. Unfortunately, no quantitative treatment of the break up of the complex has yet been published, so it is not now possible to predict the ratios of product ions where more than one product arises from a single reactant. It has, however, been observed by Lampe, et al. (41) that the ratios of secondary ions from a collision complex will often be very similar to those of the same fragment ions in the primary mass spectrum of a compound having the same composition as the complex. Thus, they pointed out that the ratio of $C_3H_5^+/C_4H_7^+$ in the reaction of C_2H_4 with C_2H_4 was about the same as that observed in the mass spectra of the butenes. The literature contains

(41) F. W. Lampe, J. L. Franklin and F. H. Field, "Progress in Reaction Kinetics," Vol. 1, Pergamon Press, New York, 1961, p. 69.

only a few examples of simple condensation reactions. This is not surprising in view of the fact that every complex is formed with enough energy to break up in either the forward or reverse direction. Since most complexes can break up very rapidly they will generally do so in a time short compared to that required to collect the ion. In a few instances such complexes have been observed to survive long enough to be measured. One example of this is given in Table 7. It might be mentioned that several apparently long lived complexes were observed by Field (37) in his study of ethylene, but these in all cases turned out to depend upon the third or higher power of the pressure, and thus were in fact complexes that had been stabilized by collision or had resulted from the decomposition of a complex of higher molecular weight.

Although the preceding discussion has largely been devoted to ions formed as bimolecular reaction products, in the last few years, many examples of ions formed with much higher pressure dependence have been observed. One of the earliest studies carried out at such elevated pressures, i.e., above 100 microns, was the study of Field (37) of ion-molecule reactions in ethylene. In this study he observed ions with pressure dependencies as high as about 6, although those exhibiting the highest pressure dependence were of such low intensity that the nature of the reactions involved could not be ascertained. Indeed, above about 3rd order the method of appearance potentials becomes completely useless, and the identification of pre-cursors to a given product becomes very tenuous indeed. To form ions at high pressures in a region from which they can be collected it is usually necessary to employ electrons of several hundred volts rather than the usual 60-70 volts employed in most mass spectrometric problems. Indeed, because of this problem, Kebarle and Hogg (45) have employed alpha particles of high energy to provide primary ions.

(45) P. Kebarle and A. M. Hogg, J. Chem. Phys. 42, 668 (1965); 43, 449 (1965)

When ions are formed by high energy massive particles it is possible to operate at much higher pressures and Kebarle (45), Wexler et al. (46) and others have

(46) S. Wexler, Assa Lifshitz and A. Guattrochi, "Ion-Molecule Reactions in the Gas Phase," Adv. in Chem. Series, Amer. Chem. Soc., Washington, D. C. 1966 p. 193

studied the ions formed at pressures up to about one atmosphere. Naturally, they have observed ions with a very high pressure dependence, although they have not been able to establish the order of reaction. With such a system, Kebarle et al. (49,50)

have observed ions having the general formula, $H^+(H_2O)_n$, with n varying from 1 to 7, and Wexler, et al. (46) have observed polymer ions from acetylene having up to 12 carbon atoms.

Recently, studies have been carried out in mass spectrometry sources at pressures up to several torr. Under these conditions, any primary ions formed will undergo many collisions and will have ample opportunity to react if they are capable of doing so. Field and Munson (47,48) have taken advantage of this to carry out some very interesting studies of reactions of higher order. They observed that in very pure methane, the principal secondary ions CH_5^+ and $C_2H_5^+$ reached a plateau and re-

(47) M.S.B.Munson and F. H. Field, _J. Am. Chem. Soc._ __88__, 2621 (1966)

(48) F. H. Field, M. S. B. Munson and D. A. Becker, "Ion Molecule Reactions in the Gas Phase," Adv. in Chem. Series, Amer. Chem. Soc., Washington, D. C. (1966), p. 167

(49) P. Kebarle and A. M. Hogg, _J. Chem. Phys._ __42__, 798 (1965)

(50) A. M. Hogg and P. Kebarle, _J. Chem. Phys._ __43__, 498 (1965)

mained constant with increases in pressure beyond about 0.5 torr. They observed also that if there were any small amount of impurities in the methane the intensities of these ions passed through a maximum around a few .10ths torr and then declined steadily with further increases in pressure. The primary ions had very small probability of colliding with anything but methane and consequently the disappearance of the secondaries must be due to their reaction with the impurities, since it is demonstrated that they did not react with methane itself. It was a simple step from this to the addition of small amounts of a variety of materials to the methane plasma, with results that proved extremely interesting. When, for example, small amounts of long chain paraffin hydrocarbons, such as dodecane, were added to the methane plasma, the spectrum of ions from the high molecular weight paraffin was quite different from that obtained by electron impact. Such high molecular weight paraffins give only small intensities of ions above about the C_5 range under electron impact. However, in the methane plasma, ions of the general composition C_nH_{2n+1} formed at each carbon number from the parent down to C_4. No doubt ions of smaller mass are also formed, but these are not observable because of the interference from secondary and ternary ions from methane. Further, the largest of these ions is the one corresponding to the parent molecules; i.e., with dodecane, $C_{12}H_{25}^+$.

Field and Munson have studied a number of compounds by this method, and in many instances have obtained profound changes in the mass spectrum, produced by "Chemical Ionization," the term which they have given the processes. (47,48) They have concluded that in the case of the methane the principal reactions are probably as follows:

$$CH_5^+ + C_nH_{2n+2} \rightarrow CH_4 + H_2 + C_nH_{2n+1}^+$$

$$C_2H_5^+ + C_nH_{2n+2} \rightarrow C_2H_4 + H_2 + C_nH_{2n+1}^+$$

$$\rightarrow C_2H_6 + C_nH_{2n+1}^+$$
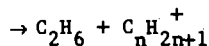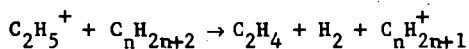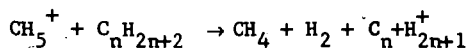
Although the previous discussion has been devoted entirely to reactions of positive ions, negative ions are also known to undergo reactions on collision. Relatively few of these reactions have been studied, however, largely because negative ions present some rather serious difficulties to the investigator. Some reactions of negative ions, however, have been carried out by Melton, Henglein and others, and several typical reactions are given in table 9.

Table 8

Some Ions Formed by Processes of Order Higher than 2

Reactant	Ionic Product	Reference
H_2O	$H^+(H_2O)_n$ (1 < n < 8)	(49)
NH_3	$H^+(NH_3)_n$ (1 < n < 5)	(50)
CH_4	$C_3H_5^+$, $C_3H_7^+$	(51)
C_2H_4	$C_4H_8^+$, $C_4H_6^+$	(37)

(51) F. H. Field, J. L. Franklin and M.S.B.Munson, <u>J. Am. Chem. Soc.</u> <u>85</u>, 3575 (1963)
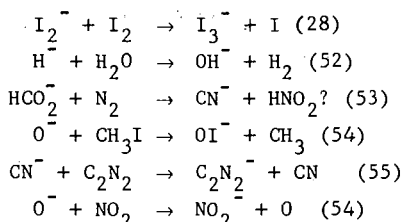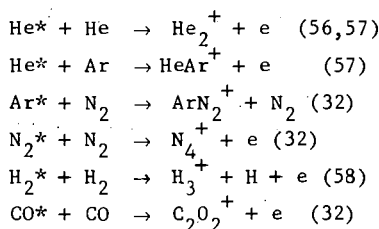
Table 9

Negative Ion-Molecule Reactions

$$I_2^- + I_2 \rightarrow I_3^- + I \quad (28)$$
$$H^- + H_2O \rightarrow OH^- + H_2 \quad (52)$$
$$HCO_2^- + N_2 \rightarrow CN^- + HNO_2? \quad (53)$$
$$O^- + CH_3I \rightarrow OI^- + CH_3 \quad (54)$$
$$CN^- + C_2N_2 \rightarrow C_2N_2^- + CN \quad (55)$$
$$O^- + NO_2 \rightarrow NO_2^- + O \quad (54)$$

(52) E. E. Muschlitz, <u>J. Appl. Phys.</u> 28, 1414 (1957)
(53) C. E. Melton and G. A. Ropp, <u>J. Am. Chem. Soc.</u> <u>80</u>, 5573 (1958)
(54) A. Henglein and G. A. Muccini, <u>J. Chem. Phys.</u> <u>31</u>, 1426 (1959)
(55) C. E. Melton and P. S. Rudolph, <u>J. Chem. Phys.</u> <u>33</u>, 1594 (1960)

Table 10

Chemi-Ionization

$$He* + He \rightarrow He_2^+ + e \quad (56,57)$$
$$He* + Ar \rightarrow HeAr^+ + e \quad (57)$$
$$Ar* + N_2 \rightarrow ArN_2^+ + N_2 \quad (32)$$
$$N_2* + N_2 \rightarrow N_4^+ + e \quad (32)$$
$$H_2* + H_2 \rightarrow H_3^+ + H + e \quad (58)$$
$$CO* + CO \rightarrow C_2O_2^+ + e \quad (32)$$

(56) J. A. Hornbeck and J. P. Molnar, <u>Phys. Rev.</u> <u>84</u>, 621 (1951)
(57) M.S.B. Munson, J. L. Franklin and F. H. Field, <u>J. Phys. Chem.</u> <u>67</u>, 1541 (1963)
(58) D. J. Keenan and E. M. Clarke, Fourteenth Annual Conference on Mass Spectrometry, Dallas, Texas, May 22-27, 1966, p. 42

Somewhat akin to ion-molecule reactions is a process first identified by Hornbeck and Molnar (56) for the formation of the rare gas diatomic ions. Hornbeck and Molnar observed diatomic ions of all the rare gases when the pressure in the ion source of their mass spectrometer was raised sufficiently. The appearance potentials of the diatomics proved to be 0.7 to 1.5 eV below the ionization potentials of the corresponding atom, and hence the diatomic ions were not derived from atomic ions. As a consequence, they proposed that excited atoms formed by electron impact reacted upon collision with a neutral atom to form a molecular ion and eject an electron, thus:

$$Ar* + Ar \rightarrow Ar_2^+ + e.$$
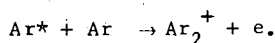
A number of investigators have subsequently studied this chemi-ionization reaction of the rare gas ions and have confirmed and extended Hornbeck and Molnar's observation. It has now been observed that all of the rare gases react with each other to form the hetero-nuclear diatomic ions (57). In addition, a number of ionic compounds of the rare gases with nitrogen, CO, O_2, methane, acetylene and others have been reported. Chemi-ionization reactions are not necessarily limited to rare gases, however. Chemi-ionization products of excited mercury atoms with a number of compounds have been observed (59) and nitrogen and CO are known to undergo chemi-ionization with their own ground state species, forming respectively N_4^+ and $C_2O_2^+$ (32).

(59) P. Cermak and Z. Herman, Tenth Annual Conference on Mass Spectrometry, New Orleans, La., 1962, p. 358.

It is natural that when both reactants and products are readily measurable consideration should early be given to the rate of the reaction. With the reaction $A^+ + M \rightarrow B^+ + S$, if M is much larger than A^+, the reaction rate is psuedo first order and the equation expressing the concentration of A^+ and B^+ is as follows:

$$\frac{A^+}{A_o^+} = e^{-kMt} \tag{1}$$

$$\frac{B^+}{A_o^+} = 1-e^{-kMt} \tag{2}$$

At relatively low pressures, (a few microns),

$$\frac{B^+}{A^+ + B^+} = kMt \tag{3}$$

A plot of $\dfrac{B^+}{A^+ + B^+}$ against M^{-1} will yield a straight line whose slope is kt. If a continuous ion withdrawal is employed, the retention time in the source will be the time required for the primary ion to drift from the point of formation in the electron beam to the exit slit under the influence of the repeller potential. The time is thus:

$$\left(\frac{2\ md}{eE}\right)^{1/2}$$

where E is the field strength, m is the mass of the ion, and d the distance from the center of the electron beam to the ion exit slit. With the slope known, k can be calculated and a large number of rate constants have been determined in this way.

Lampe, Franklin and Field (41) discussed this problem of rates of ion molecule reactions at some length, and surveyed the known data at that time. A few typical rate constants for second order ion-molecule reactions are given in table 11. It will be observed that many of them are in the order of 10^{-9} cc/molecule/sec. However, values as small as 10^{-13} cc/molecule/sec have been reported for some reactions. The values in the neighborhood of 10^{-9} cc/molecule/sec represent reactions that must occur at essentially every collision in that they have cross sections considerably larger than ordinary collision cross sections. The values around 10^{-13} represent about the limit at which secondary ions can be measured with sufficient confidence to justify calculation. It is obvious that reactions of this kind occurring at relatively low pressures and in times of the order of a micro-second must be very fast reactions, and in fact, so fast that the activation energy must be either 0 or very small. As was mentioned before, ion-molecule reactions to be observable must not involve appreciable energy of activation. Stevenson and Schissler (4,11) have confirmed this experimentally for a few reactions and the very fact that a reaction is observed precludes this possibility. It should be mentioned, however, that certain endo-thermic reactions can be forced to take place if the relative

velocity of the reacting partners is sufficiently great. Giese and Maier (60) have shown that for the reaction $Ar^+ + CO \rightarrow Ar + C^+ + O$, which is endothermic by 6.62 for the $2P_{3/2}$ state and 6.44 eV for the $2P_{1/2}$ state of Ar^+, the threshold for the appearance of C^+ is:

$$\frac{6.44 \times \left(M_{Ar} + M_{CO}\right)}{M_{CO}} \quad \text{or} \quad 15.65 \text{ eV.}$$

Their measured values were in agreement with this relation.

(60) C. F. Giese and W. B. Maier, J. Chem. Phys. 39, 197 (1963)

Table II
Some Second-Order Rate Constants

Reaction	10^{10}k, cc/molecule sec	Reference
$D_2^+ + D_2 \rightarrow D_3^+ + D$	14.5	4,11
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	10	61,62,63
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	12.7	1,2,13
$C_2H_3^+ + C_2H_6 \rightarrow C_3H_5^+ + CH_4$	14.5	9
$O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H$	0.126	22
$CH_4^+ + O_2 \rightarrow CH_3O^+ + OH$	0.257	22

(61) V. L. Tal'roze and E. L. Frankevich, J. Phys. Chem. USSR 34, 1275 (1960)

(62) C. W. Hand and H. von Weyssenhoff, Can. J. Chem., 42, 195, 2385 (1964)

(63) J. L. Franklin, Y. Wada, P. Natalis and P. M. Hierl, J. Phys. Chem. 70, 2353 (1966)

All reaction rate studies have not been limited to extremely low pressures. When the pressure in the ion source becomes sufficiently great the reactions follow the psuedo first order rate laws over rather wide ranges of pressure, unless subsequent reactions interfere. Thus, Field et al. (51) found the disappearance of CH_4^+ in methane to obey first law kinetics over a pressure range of about 0.1 to 400 Torr. However, as the pressure is raised, in certain systems, reactions of a higher order do occur. Field, (37) studying ethylene, has reported some reactions having apparent orders as high as about 6. These, of course, are not truly 6th order reactions, but simply represent a succession of perhaps five secondary reactions which show dependence upon the 6th power of the pressure. Rates of reactions of such high order do not yield satisfactory rate constants, but it has been possible to determine rate constants for reactions of 3rd order, and Field and several others have made approximate measurements of the rate constants for such third order processes. As is the case with the second order processes, these reaction rates are relatively high. For example, in ethylene, Field determined several third order rate constants to be in the order of 10^{-27}cc^{2}molecule^{-2}sec^{-1}.

Although most of the measurements of rate constants in the literature were obtained with the source operating in a continuous mode employing a variation in pressure to establish the rate, some studies have been made in which retention time in the source was varied. Such measurements were originally made by Tal'roze and Frankevitch (61), but subsequent measurements have been made by Hand and von Weissenhoff (62) and Franklin, Natalis, Wada, and Hierl (63). In order to obtain a satisfactory variation of time, a pulsed mode is employed. In such an operation a pulse of electrons is fired through the gas. After it is stopped, the resulting ions can be retained in the source for a controlled period of time and then rapidly extracted by a pulse of high energy. By varying the delay time, the time of retention in the source is varied, and rate constants determined in the manner more usually employed by chemists in rate studies. Results obtained in this way generally agree

rather well with those obtained by the pressure method, although some differences have been observed. One difference that may be of significance is that the ions in the pulsed mode will generally have approximately thermal energies, whereas those reacting in the continuous mode will have variable energies, depending upon the point of their reaction in travelling from the electron beam to the exit slit.

The question of the effect of ionic energy on reaction rate has been one of considerable interest and the subject of a number of investigations, both theoretical and experimental. In their early work on ion-molecule reactions, Franklin, Field and Lampe (3) observed that when they varied the field strength in the ion source in order to vary the retention time, the rate constants that they calculated for their ion-molecule reactions varied considerably. In general, they seemed to drop as the field strength increased, suggesting that the reaction rate constant decreased with the relative velocity of ions and neutrals. Other investigators have made similar observations. However, it appears that not all reactions show such reduction in rate constants with increasing relative velocity. Attempts to explain this have been made by a number of investigators. Field, Franklin and Lampe (3) attempted to obtain the theoretical relations based upon a balance of polarization and centrifugal forces. Gioumousis and Stevenson (64) derived a more precise expression

(64) Gioumousis, G. and Stevenson, D. P., J. Chem. Phys., 29, 294 (1958)
(65) P. Langevin, Ann. Chim. Phys. 5, 245 (1905)

for the collision rate based upon Langevin's (65) treatment for polarizable systems. Gioumousis and Stevenson found the collision cross section to be:

$$\sigma = \frac{2e\pi}{v_i} \left(\frac{\alpha}{\mu}\right)^{1/2} \qquad (4)$$

where α is the polarizability of the neutral, v_i is the velocity of the ion, μ is the reduced mass and e the charge on the electron. Since

$$v_i = \left(\frac{2E}{m_i}\right)^{1/2}$$

σ will vary as $E^{-1/2}$. Further, since $k = \sigma v$

$$k = 2e\pi\left(\frac{\alpha}{\mu}\right)^{1/2} \qquad (5)$$

and thus is independent of velocity or energy. This, unfortunately, did not agree with the observed rate behavior of a number of reactions, although it appears to hold for some. In fact, Field, et al. (3) studied the effect of field strength upon rate constant and found that for several reactions k decreased with increasing field strength. Hamill and his associates (66,67) have shown that ion-molecule reactions cannot be accurately treated as involving point particles. By considering the de-

(66) N. Boelrijk and W. H. Hamill, J. Am. Chem. Soc. 84, 730, (1962)
(67) D. A. Kubose and W. H. Hamill, J. Am. Chem. Soc. 85, 125 (1963)

formable neutral to exhibit a hard core to high energy collisions while being deformable in low energy collisions, these workers showed that for small ion energies σ obeyed the Gioumousis-Stevenson relation (equation 5), but for large energy $\sigma \propto E^{-1}$ which agrees with experimental results. Theard and Hamill (68) and Moran and Hamill (69) have extended their treatment to ion-molecule reactions involving

(68) L. P. Theard and W. H. Hamill, J. Am. Chem. Soc. 84, 1134 (1962)
(69) T. F. Moran and W. H. Hamill, J. Chem. Phys. 39, 1413 (1963)

neutrals with permanent dipoles. They showed that at low relative velocities a cross section for the ion-permanent dipole interaction,

$$\sigma_D = \frac{\pi e \mu}{E_t}$$

must be added to the Langevin cross section. Here μ is dipole moment and E_t is the translational energy of the reacting system in center of mass coordinates.

No attempt will be made here to review all of the studies of the effect of energy upon the rates of ion-molecule reactions. However, several investigators who have made especially important contributions should be mentioned. In addition to the work of Hamill discussed above, important studies have been made by Futrell and Abramson (70), Giese and Maier (71), Friedman (72,73) and Light and Horrocks (74).

(70) J. H. Futrell and F. P. Abramson, "Ion-Molecule Reactions in the Gas Phase," Adv. in Chem. Series 58, Amer. Chem. Soc., 1966, p. 107.
(71) C. F. Giese and W. B. Maier, J. Chem. Phys. 39, 197, 739 (1963)
(72) T. F. Moran and L. Friedman, J. Chem. Phys. 39, 2491 (1963); 42, 2391 (1965)
(73) F. S. Klein and L. Friedman, J. Chem. Phys. 41, 1789 (1964)
(74) J. C. Light and J. Horrocks, Proc. Phys. Soc. 84, 527 (1964)

It should be pointed out that if the relative velocities of ions and neutrals become sufficiently high other reactions begin to occur as a result of the different forces coming into play. Thus a fast moving ion passing a molecule with sufficient velocity may simply strip off a peripheral atom, leaving the partially denuded entity behind. Such stripping reactions have been studied by Henglein (75) and Koski (76), who found that they obey quite different rules from those above. It thus

(75) A. Henglein, "Ion Molecule Reactions in the Gas Phase," Adv. in Chem. Series 58, Amer. Chem. Soc., Washington, D. C., p. 63
(76) M. A. Berta, B. Y. Ellis and W. S. Koski, ibid., p. 80

appears that a complete theory of the rates of ion-molecule reactions has not been developed, but there is little doubt that to a first approximation the equation of Gioumousis and Stevenson gives fairly good results. It is also true that the reactions tend to be quite fast, and this becomes a matter of overriding importance in many processes involving ions. Thus is has been shown by Lampe (77,78) and by Futrell (79) that ion-molecule reactions are the controlling factor in certain

(77) F. W. Lampe, Radiation Research 10, 671 (1959)
(78) F. W. Lampe, J. Am. Chem. Soc., 82, 1551 (1960)
(79) J. H. Futrell, J. Am. Chem. Soc. 81, 5921 (1959)

radiation induced processes involving paraffin and olefin hydrocarbons.

An electric discharge of course involves ions and electrons and the ions present can be sampled and analyzed by mass spectrometry. Such studies have been undertaken by a number of investigators and some progress is being made toward understanding the chemical behavior of ions in various discharges. The problem is complicated by the fact that there are several kinds of electric discharge, each of which has its own physical and chemical characteristics. Of these, the type most often studied is the direct current glow discharge, but corona and high frequency and micro-wave discharges have also received some attention.

In order to analyze the ionic content of a discharge it is necessary to transfer the ions from the discharge into the mass analyzer. While this is not a particularly serious problem at pressures below 10 microns, the difficulty becomes more acute as the pressure increases. This is attributable to the fact that electrons and ions diffuse to the walls at different rates, so that an electric gradient is established which alters the distribution of energy of the various charged species. Ordinarily a sheath of ions is formed at any surface, including that of a sampling probe and ions or electrons must have, or be given enough energy to pass through this sheath in order to be sampled. However, if the energy is sufficiently high some ions may be decomposed by collision. The result then is that there is often

considerable undertainty as to the quantitative correspondence of the ion distribution reported by the mass spectrometer with the actual distribution in the discharge. Further, while there is little doubt that the ions observed were actually present, there is always some question as to the presence of ions that might be expected, but that are not observed.

An added complication that must be taken into account, especially in glow discharges, is that different portions of the discharge have different characteristics. Thus the negative glow and positive column have quite different electric fields, the ions and electrons present have different energies and the distribution of ions in the two regions is different.

In spite of these reservations, considerable information has been obtained concerning the ions present in certain discharges and some understanding of the reactions occurring is beginning to develop.

In the glow discharge, the regions most studied have been the negative glow and the positive column. Both are regions of nearly equal positive and negative ion concentration, although the ion concentration in the negative glow is usually greater (often 10-100 times) than that in the positive column. Further, the electric field in the negative glow is considerably greater than that of the positive column, through which the ions drift with relatively small energies.

Discharges in the rare gases, of course, always contain atomic ions and, at sufficiently high pressures, diatomic ions as well. This latter can be produced by two possible reactions, typified by helium:

$$He^* + He \rightarrow He_2^+ + e \qquad (6)$$

$$He^+ + 2He \rightarrow He_2^+ + He \qquad (7)$$
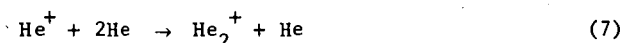
Since the formation of He* is an excitation process it will occur over a relatively small energy range with electrons of energy close to the ionization potential of He. Thus, it would be expected to predominate in the positive column of a glow discharge. This has been observed by Morris (80) and by Pahl (81,82).

(80) D. Morris, Proc. Phys. Soc. (London) A68, 11 (1955)

(81) M. Pahl and U. Weimer, Z. Naturforsch 13a, 753 (1958)

(82) M. Pahl, Z. Naturforsch, 14a, 239 (1959)

In order for reaction 7 to be observed relatively high pressures are required. The third order rate constant will probably not exceed 10^{-30} cc^2/molecule^{2}second and the time of the ion in the plasma will probably not exceed 10^{-3} seconds. Thus, for He_2^+/He^+ to be approximately 0.1 by reaction 7 the pressure must be approximately 5 Torr. Thus the formation of the diatomic ion by the three-body process will decrease very rapidly with decreasing pressures and will be negligible below 0.1 Torr. Knewstubb and Tickner (83) have studied the ions of the rare gases in both the negative

(83) P. F. Knewstubb and A. W. Tickner, J. Chem. Phys. 36, 674, 684 (1962)

glow and the positive column of a dc glow discharge. They find the ratio Ar_2^+/Ar^+ to be much less in the negative glow than in the positive column, and conclude that the diatomic ion is formed principally by the three body process in the negative glow, but that the chemi-ionization reaction predominates in the positive column. Similar considerations apply to the other rare gases.

In our laboratory a microwave discharge was generated in helium by a 100 watt Raytheon microtherm generator and sampled through a pinhole leak at the apex of a conical probe into a quadrupole mass filter. The intensity of the He^+ ion dropped exponentially in the range studied from a relative intensity of unity at 0.1 Torr to about .002 at 0.5 Torr.

In the same pressure range He_2^+ increased in intensity from 0.002 at 0.1 Torr to a broad maximum around 0.3 Torr and then declined rapidly at higher pressures. If the He_2^+ is formed by the three-body process (equation 7) the rate constant would have to be about 10^{-28} cc^2/molecule^2/sec. which seems excessive. We conclude then that the diatomic ion is probably formed principally by the chemi-ionization process. (equation 6).

Of perhaps greater interest are the ionic processes occurring in more complex gases. Thus, glow discharges in hydrogen (84,85) and in H_2-D_2 mixtures (86) showed

(84) C. J. Braesfield, Phys. Rev. 31, 52 (1928)
(85) O. Luhr, J. Chem. Phys. 3, 146 (1935)
(86) H. D. Beckey and H. Dreeskamp, Z. Naturforsch 9a, 735 (1954)

the formation of H_3^+ or H_3^+ - D_3^+ mixtures, which increased in concentration with pressure at the expense of the diatomic ion. In an effort to interpret the behavior of the discharge in hydrogen, Eyring, Hirschfelder and Taylor (87) considered the

(87) H. Eyring, J. O. Hirschfelder and H. S. Taylor, J. Chem. Phys. 4, 479 (1936)

reaction forming H_3^+ to be:

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{8}$$

They took the activation energy for the reaction to arise from the balance of centrifugal force and polarization attraction acting in opposite directions. The resulting rate constant for the reaction is:

$$k = 2\pi e \left(\frac{\alpha}{\mu}\right)^{1/2}$$

i.e., the same as equation 5. Subsequent studies of this reaction in a mass spectrometer ion source (4) have established this reaction beyond doubt, and have shown that the reaction rate is given approximately by the above relation of Eyring, et al. Recent studies by Ortenburger et al. (88) employing a high frequency discharge have

(88) I. B. Ortenburger, M. Hertzberg and R. A. Ogg, J. Chem. Phys. 33, 579 (1960)

shown that reaction 8 occurs under these conditions as well.

Studies of ions in the negative glow and Faraday dark space of a glow discharge in water vapor at 0.4 Torr have been made by Knewstubb and Tickner (89). They

(89) P. F. Knewstubb and A. W. Tickner, J. Chem. Phys. 38, 464 (1963)

found the maximum ion intensity to occur in the negative glow. There was little H_2O^+ present, but a series of solvated protons was observed having the general composition $H^+(H_2O)_n$ with n varying from one to five. Mass spectrometer studies have established the reaction: (1,2,13)

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \tag{9}$$

and more recent studies have detected the more highly solvated species. (49,50) The results of the discharge studies showed the first four water molecules to be more strongly bonded to the proton than succeeding molecules and this has been substantiated by the work of Kebarle (49,50) previously discussed.

Similar studies have been made of ions in a glow discharge in ammonia (90)

(90) P. H. Dawson and A. W. Tickner, $\underline{J}$. Chem. $\underline{Phys}$. $\underline{40}$, 3745 (1964)

with similar results. The negative glow at 0.4 Torr was found to contain the ions $H^+(NH_3)_n$ with n from 1 to 5, with NH_4^+ being formed in highest concentration in the negative glow, but with $H^+(NH_3)_4$ predominating in the Faraday dark space. The multiply solvated proton has also been observed in the ion source of a mass spectrometer at elevated pressure. (91, 92)

(91) A. M. Hogg and P. Kebarle, $\underline{J}$. Chem. $\underline{Phys}$. $\underline{43}$, 449 (1965)

(92) A. M. Hogg, R. M. Haynes and P. Kebarle, $\underline{J}$. $\underline{Am}$. Chem. $\underline{Soc}$. $\underline{88}$, 28 (1966)

Knewstubb (93) also mentions the observation of ions in a glow discharge in

(93) P. F. Knewstubb, "Mass Spectrometry of Organic Ions," Academic Press, New York, 1963, p. 284

methane in which the ions $C_2H_5^+$ and CH_5^+ predominated, and in which some 40% of the ions present contained three or more carbon atoms. This is quite different from the results obtained by Munson and Field (47, 48) for studies of methane at elevated pressures. They found that with quite pure methane at pressures above about 1 Torr the CH_5^+ and $C_2H_5^+$ ions were present in the same ratio as CH_4^+ and CH_3^+ (the precursors) in the primary mass spectrum of methane, and that ions having more than two carbon atoms were present in only minor proportions. This suggests that the ions of higher mass reported by Knewstubb (93) originated either from impurities in the methane employed or, more probably, from molecules such as acetylene or ethylene formed by the action of the discharge on methane.

Nitrogen has been the subject of several investigations employing both mass spectrometer ionization chambers and discharges for the production of ions. The ions of greatest interest are N_3^+ and N_4^+. The mass spectrometer studies have shown N_3^+ to be formed by the reaction:

$$N_2^{+*} + N_2 \rightarrow N_3^+ + N$$
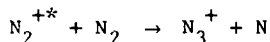
where N_2^{+*} implies an excited ion having an appearance potential of about 21-22 eV. (31,32,33) N_4^+ has been found to result from the reaction:(94)

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2 \tag{11}$$

(94) G. Junk and H. J. Svec, $\underline{J}$. $\underline{Am}$. Chem. $\underline{Soc}$. $\underline{80}$, 2908 (1958)

In addition, Munson et al. (32) showed that under certain conditions N_4^+ is formed by the chemi-ionization reaction:

$$N_2^* + N_2 \rightarrow N_4^+ + e \tag{12}$$

Both ions have been observed in electric discharges in nitrogen. Luhr (95) and Dreeskamp (96) found N_3^+, but it appeared to be formed only in the drift space

(95) O. Luhr, $\underline{Phys}$. $\underline{Rev}$. $\underline{44}$, 459 (1933)
(96) H. Dreeskamp, $\underline{Z}$. $\underline{Naturforsch}$ $\underline{12a}$, 876 (1958)

following the discharge. It was thought to result from the reaction

$$N^+ + 2N_2 \rightarrow N_3^+ + N_2 \tag{13}$$

Shahin (97) has reported N_3^+ formed in a glow discharge at 0.3 Torr in nitrogen

(97) M. M. Shahin, "Ion-Molecule Reactions in Gases," Advances in Chemistry Series No. 58, American Chemical Society, Washington, D. C., 1966 p. 315

as well as N_4^+ in a corona discharge in a mixture of nitrogen and water vapor. The relative intensity of N_4^+ passed through a maximum at about 10 Torr, then slowly declined at higher pressures. Shahin attributed the formation of the ion to the reaction:

$$N_2^+ + N_2 \rightarrow N_4^+ \tag{14}$$

In the same system he observed H_2O^+, H_3O^+, $H_5O_2^+$ and N_2H^+ ions, all apparently resulting, at least in part, from reaction of N_2^+ with water.

In this laboratory nitrogen has been passed through a microwave discharge at pressures of 0.01 to 0.3 Torr and the plasma sampled into a quadrupole mass filter where the ions were separated and analyzed. N_4^+ was not observed at any condition studied. N_3^+ was formed in very small concentrations (about 1% of N_2^+) at 0.01 Torr, but increased rapidly in intensity, passing through a broad maximum at about 0.15 - 0.20 Torr, and then decreasing at higher pressures. In the same pressure range the intensity of N_2^+ dropped precipitously from 90 to 1.5, and that of N^+ remained constant at about 9, all in arbitrary units. At the N_3^+ maximum all of the ions were of nearly equal intensity. A brief study of the variation of the intensities of these ions with nominal power input at a pressure of 0.15 Torr showed N_2^+ and N^+ to decrease in intensity with decreasing power until the discharge was extinguished at about 40% of maximum. These curves were reminiscent of an ionization efficiency curve, and strongly suggest the average electron energy decreased with decreasing power input. The N_3^+ ion increased in intensity with decreasing power input up to a broad maximum between 75 and 65% of maximum power, after which it again decreased. This suggests that an excited state is formed by electron impact with electrons of broad energy spread. Such an energy spread has been found in our studies, and will be reported separately. Further, we find that the electrons possess an approximately Maxwell-Baltzmann distribution of energy, and that the average energy decreases as the pressure increases, in accordance with our observation of the variation of N_3^+ with pressure. This also accounts in part for the decrease in N_2^+ with pressure.

The near constancy of N^+ with increasing pressure is difficult to understand. The number of N^+ ions formed by direct electron impact upon N_2 or N must be relatively small and can hardly account for the intensity of the N^+ observed. It is possible that at the higher pressures most N^+ is formed by the reaction:

$$N_2^+ + N \rightarrow N^+ + N_2 \tag{15}$$

but this is, of course, speculative.

The absence of N_4^+ is puzzling, since it has been observed in some discharges. It is possible the ion is destroyed in passing through the sampling probe. This seems unlikely, however, since N_4^+ is held together by a bond of about 1.5 eV energy. This is about the same strength as the bond in He_2^+, which we observe. Conceivably, the ion may appear at higher pressures, but some alterations in our sampling probe will be necessary to achieve this.

Several investigations of ions in glow discharges in oxygen have been reported. O^+ and O_2^+ were reported by Knewstubb (93), Luhr (98) and Dickenson and Sayers (99).

(98) Luhr, O., Phys. Rev. 38, 1730 (1931)

(99) P. H. G. Dickenson and J. Sayers, Proc. Phys. Soc. (London) A76, 137 (1960)

In addition, O_3^+ and O_4^+ (99) have been reported.

In our studies of oxygen in the pressure range 0.01-0.3 Torr, using a microwave discharge only O^+ and O_2^+ were found. Both ions dropped in intensity exponentially with increasing pressure, but the O^+ dropped slightly less rapidly than did O_2^+

The drop in 0^+ with increasing pressure may be due to the fact that 0^+ can react with 0_2 by charge exchange.

$$0^+ + 0_2 \rightarrow 0_2^+ + 0 \tag{16}$$

This would account for the drop in 0^+ intensity at conditions at which N^+ (which cannot undergo loss by charge exchange) remains constant. In the same pressure range, 0_2^+ drops in intensity to about the same extent as does N_2^+, which can disappear by charge exchange with N.

In a mass spectrometer ion chamber 0_3^+ and 0_4^+ are found in rather small intensities, apparently formed by the reactions:

$$0_2^+ \quad {}^2\pi_u + 0_2 \rightleftarrows 0_4^{+*} \rightarrow 0_3^+ + 0 \tag{17}$$

$$0_4^{+*} + 0_2 \rightarrow 0_4^+ + 0_2 \tag{18}$$
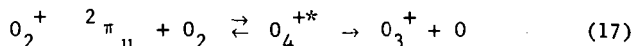
The latter is very faint, however. The ionization potential of 0_3 is slightly greater than that of 0_2 (100,101), so 0_3^+ can react with 0_2 as follows:

$$0_3^+ + 0_2 \rightarrow 0_2^+ + 0_3 \tag{19}$$

(100) J. T. Herron and H. I. Schiff, <u>J. Chem. Phys.</u> <u>24</u>, 1266 (1956)

(101) R. K. Curran, <u>J. Chem. Phys.</u> <u>35</u>, 1849 (1961)

No doubt this accounts for the failure to observe 0_3^+. The absence of 0_4^+ may be merely a matter of sensitivity.

In our laboratory we have also studied the ions formed in a microwave discharge in a mixture of nitrogen and oxygen at a constant pressure of about 0.1 Torr. As might be expected, the intensities of N_2^+ and N^+ decreased and those of 0_2^+ and 0^+ increased as the proportion of nitrogen decreased and that of oxygen increased. NO^+ was very intense over the range of 10% to 75% oxygen in the mixture. This is not surprising, since N^+, N_2^+ and N_3^+ reacting with 0_2 or 0 and 0^+ and 0_2^+ reacting with N or N_2 are capable of producing NO^+. Further, NO is produced in the discharge and no doubt is ionized by electron impact.

Small amounts of NO_2^+ ions were observed in all of the mixtures studied, and small amounts of N_2O^+ were found in the nitrogen rich mixtures, but disappeared when the proportion of nitrogen in the mixture dropped below 75%. The manner of their formation is not known, but from their very small intensity we infer that they are probably formed by third order processes. It is surprising that no N_3^+ ion was observed when oxygen was present. Presumably it is capable of reacting in several ways with 0_2 or 0, and so is destroyed as fast as it is formed. The system 0_2-N_2 is of great interest and will be studied further.